Dioxins and Furans in Bed Sediment and Fish Tissue of the Willamette Basin, Oregon, 1992–95

Water-Resources Investigations Report 97–4082–D

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Front cover photograph: The Willamette River flows through Portland before entering the Columbia River.

Back cover photographs: Upper, Bernie Bonn processes a sample in a mobile water quality laboratory near Corvallis; center: fish from the Willamette River at Portland are kept in live wells before processing for analysis; lower, bed sediment from Mack Creek is sieved in the field prior to analysis.

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ABBREVIATIONS

Abbreviation	Unit	Abbreviation	Unit
Concentration units		*Miscellaneous units*	
µg/g	microgram per gram	cm	centimeter
mg/L	milligram per liter	°C	degree Celsius
pg/g	picogram per gram	L	liter
peq/g	picoequivalent per gram	mL	milliliter
		mm	millimeter

Dioxins And Furans In Bed Sediment And Fish Tissue Of The Willamette Basin, Oregon, 1992–95

By Bernadine A. Bonn

U.S. Geological Survey
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SIGNIFICANT FINDINGS

- Dioxins and furans were found in bed sediment and fish tissue throughout the Willamette Basin, including samples from the most remote sites.
- The highest concentrations in bed sediment were found at sites where industrial or urban inputs were most likely; potential toxicity at these sites (as measured by toxicity equivalents concentration) was high enough to be associated with increased risk to sensitive mammalian wildlife.
- From 30 to 60 percent of the toxicity equivalents concentration in bed sediment was due to hepta- and octa- congeners, not 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin), which was detected at only 6 of 22 sites.
- Compared to bed sediment from the same site, fish tissue usually had lower total concentrations of dioxins and furans, but contained a higher proportion of the most toxic congeners, such as 2,3,7,8-TCDD and 2,3,7,8-TCDF (2,3,7,8-tetrachlorodibenzofuran).
- Concentrations of dioxins and furans in bed sediment at most sites in agricultural and forested areas were similar to those at reference sites worldwide and are probably background concentrations due to atmospheric deposition.

WHAT ARE DIOXINS AND FURANS?

Dioxins and furans, or more properly polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), are families of related chemical compounds that are of interest because of their potential toxicity.

The basic structures of dioxins and furans are shown in figure 1. Compounds may differ in the number of chlorine atoms that they contain (from one to eight) and in the relative positions of those chlorine atoms. Each different compound is called a congener. In all, there are 75 dioxin congeners and 135 furan congeners. Congeners that contain the same number of chlorine atoms form a congener class and are called homologs. The conventions for naming homologs and the abbreviations used in this report are summarized in table 1. Individual congeners are distinguished by including the position numbers of the chlorine atoms (fig. 1) at the beginning of the name or abbreviation, for example, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

Dioxins and furans share similar properties. They have low water solubility and tend to prefer organic phases, such as humus and lipid, to water. Water solubility decreases as the number of chlorine atoms increases. The least soluble congener is OCDD; its solubility is estimated to be 7×10^{-7} mg/L (Mackay and others, 1992). The eventual sink for these compounds is thought to be sediment, where their estimated half-lives exceed 5 years (Mackay and others, 1992).

The toxicity of dioxins and furans differs among congeners. The most toxic congener is 2,3,7,8-TCDD. In general, congeners that have chlorine atoms in the 2, 3, 7, and 8 positions are more toxic than the others. Toxicity decreases as the number of chlorine atoms increases or decreases from four. To assess the overall toxicity of these compounds, dioxin and furan concentrations are commonly converted into units of toxicity equivalents. This conversion is done by multiplying the concentration of each 2,3,7,8-congener by its toxicity equivalence factor (table 2), which converts the concentration of the 2,3,7,8-congener into an estimated equivalent concentration of 2,3,7,8-TCDD. It should be noted that the use of toxicity equivalence factors is not limited to dioxins and furans, but may be applied to other compounds, such as coplanar polychlorinated biphenyls (PCBs), which are thought to act by the same mechanisms as dioxins and furans. Consequently, a toxicity equivalents concentration (TEC) may include significant contributions from compounds other than dioxins or furans. TECs in this report are limited to contributions from dioxins and furans.

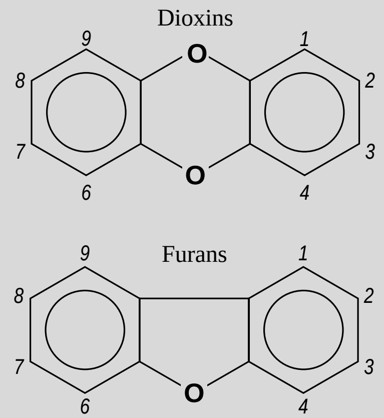

FIGURE 1. Basic structures of dioxins and furans. Each compound may contain from one to eight chlorine atoms located in the positions indicated by the numbers 1–4 and 6–9.

The toxicity of dioxins and furans varies widely among animal species. The dioxin congener 2,3,7,8-TCDD became known as the “most toxic man-made chemical” because of its acute toxicity to guinea pigs; it is, however, 10,000 times less toxic to hamsters than to guinea pigs (Hites, 1990). In aquatic environments, fish are more sensitive to dioxins and

TABLE 1. Naming conventions, abbreviations, and congener information for tetra- through octa- dioxin and furan congener classes

Number of Chlorine Atoms	Prefix	Congener Class Name	Abbreviation	Number of Congeners in Class
4	tetra	tetrachlorodibenzo-*p*-dioxin	TCDD	22
		tetrachlorodibenzofuran	TCDF	38
5	penta	pentachlorodibenzo-*p*-dioxin	PeCDD	14
		pentachlorodibenzofuran	PeCDF	28
6	hexa	hexachlorodibenzo-*p*-dioxin	HxCDD	10
		hexachlorodibenzofuran	HxCDF	16
7	hepta	heptachlorodibenzo-*p*-dioxin	HpCDD	2
		heptachlorodibenzofuran	HpCDF	4
8	octa	octachlorodibenzo-*p*-dioxin	OCDD	1
		octachlorodibenzofuran	OCDF	1

TABLE 2. Toxicity equivalence factors for dioxin and furan congeners

[Toxicity equivalence factors are those recommended by the U.S. Centers for Disease Control and provided in USEPA Method 8290 (U.S. Environmental Protection Agency, 1990). Toxicity equivalence factors for non-2,3,7,8-congeners are assumed to be zero]

Dioxins		Furans	
Congener[a]	Toxicity Equivalence Factor	Congener	Toxicity Equivalence Factor
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	0.5	1,2,3,7,8-PeCDF	0.05
		2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,7,8,9-HxCDF	0.1
		2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
OCDD	0.001	OCDF	0.001

[a] A dioxin counterpart does not exist for every furan congener because the dioxin structure is more symmetric than the furan structure. For example, the furans 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF are different isomers, whereas the dioxins 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDD are identical, and therefore the name 2,3,4,7,8-PeCDD is not used.

Dioxins and furans are not deliberately manufactured, but are inadvertently produced as by-products from two types of reactions: combustion of chlorinated organic compounds and chlorination of aromatic compounds. Processes that produce PCDD/Fs include municipal and medical waste incineration, wood burning, production of chlorinated aromatic compounds, bleaching of kraft pulp, metals production, and chlorination of sewage effluent. Because chlorinated organic compounds are used in the manufacture of a variety of products (such as wood preservatives, pesticides, and dyes), those products also may contain trace amounts of dioxins and furans.

furans than are aquatic invertebrates or amphibians, and fish fry are more sensitive than adult fish (U.S. Environmental Protection Agency, 1993). Recently, concern has focused on the ability of these compounds to affect reproduction by interfering with the normal functioning of hormones. The U.S. Environmental Protection Agency also considers dioxins and furans to be human carcinogens (U.S. Environmental Protection Agency, 1993). The risks of various environmental concentrations of 2,3,7,8-TCDD are shown in table 3.

TABLE 3. Risks of various environmental concentrations of 2,3,7,8-TCDD

[Data from U.S. Environmental Protection Agency (USEPA) (1991, 1993). Abbreviations defined as follows: pg/g, picogram per gram; <, less than; >, greater than]

Organism	Concentration in Fish (pg/g wet weight)	Concentration in Sediment (pg/g dry weight)
Low risk to sensitive organisms[a]		
Fish	50	60
Mammalian wildlife	0.7	2.5
Avian wildlife	6	21
High risk to sensitive organisms[b]		
Fish	80	100
Mammalian wildlife	7	25
Avian wildlife	60	210
Human health criteria		
No serious health concerns related to fish consumption[c]	< 25	
Restrict consumption to twice per month[c]	25–50	
Consumption not recommended[c]	> 50	
Concern for soil in residential areas[d]		100

[a] "Low risk to sensitive organisms" is defined by the USEPA as the "highest concentration that is unlikely to cause significant effects."
[b] "High risk to sensitive organisms" is defined by the USEPA as the "lowest exposure concentration that will likely cause severe effects."
[c] Criteria developed by U.S. Food and Drug Administration for fish caught in the Great Lakes for use in interstate commerce only.
[d] Criteria developed by the U.S. Centers for Disease Control.

The purpose of this study was to assess the occurrence and distribution of the tetra- through octa- dioxin and furan congeners in the Willamette and Sandy River Basins (hereafter, the Willamette Basin), Oregon. Because these compounds are extremely hydrophobic, bed sediment and fish tissue were the media sampled.

The Oregon District of the U.S. Geological Survey (USGS) began this work in 1992 in cooperation with the Oregon Department of Environmental Quality (ODEQ). Guidance and initial funding were provided through the Willamette River Technical Advisory Steering Committee, a group composed of representatives from local industries, environmental organizations, and governmental agencies. The initial phase was completed in 1992 (Anderson and others, 1996).

The USGS continued this work from 1993–1995 as part of the Willamette Basin National Water-Quality Assessment (NAWQA). The NAWQA Program was designed to assess the water quality of representative watersheds nationwide, including current status, long-term trends, and the effects of both natural and human factors (Gilliom and others, 1995). Although PCDD/Fs were not target analytes for the NAWQA Program, they were of enough local concern that the Willamette Basin study group included them in its bed sediment and tissue sampling (Wentz and McKenzie, 1991).

Sample Collection and Processing

Bed sediment samples were collected from 22 sites in the Willamette Basin; fish tissue samples were collected from 8 sites. (fig. 2, table 4). The sites were chosen to represent a cross-section of hydrology, basin scale, and land use. Five forested sites represented background conditions. Some sites, such as Zollner Creek, were located in basins dominated by agricultural land use. Several sites with known water-quality problems were sampled, including A-3 Channel and

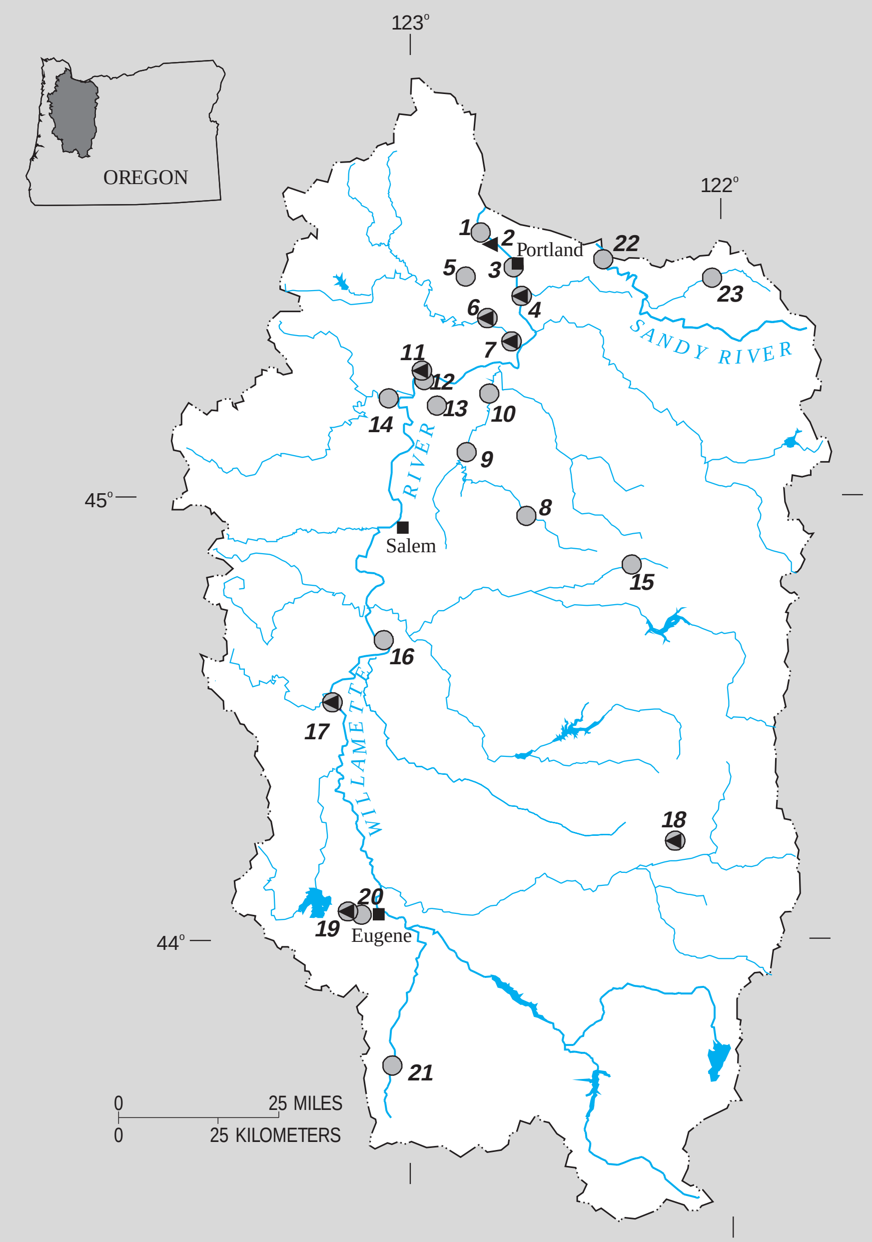

FIGURE 2. Locations of sampling sites. Samples types are: ○ bed sediment, ◀ fish tissue, and ◀ both bed sediment and fish tissue. (See table 4 for site names and sample details.)

Middle Fourth Lake. The main stem Willamette River was sampled at river mile (RM) 137 (near Corvallis), RM 55 (near Newberg), and in the Portland Harbor area (RMs 5, 7, and 13).

BED SEDIMENT— At wadeable sites, the top 1–2 cm of fine grained sediment was collected using a Teflon scoop. Sediment was sampled from several depositional zones within a reach and composited. About 8 L of wet sediment were collected from each site. The same approach was used for non-wadeable sites, except that the method was applied to sediment sections that had been obtained using an Ekman dredge. An approximate 300-mL subsample was sieved at 2 mm and kept at 4 °C until analysis. The sediment collection method is described in detail by Shelton and Capel (1994).

FISH TISSUE— Fish were collected by electrofishing and euthanized by a sharp blow to the head. Species collected are shown in table 4. In general, the choice of species was based on availability. Each sample consisted of 5–20 whole fish, which were wrapped in aluminum foil and frozen until analysis. The fish were homogenized and then subsampled by Quanterra Environmental Services (Sacramento, California).

CHEMICAL ANALYSES

Samples were analyzed for 10 tetra- through octa- dioxin and furan homolog totals, 17 individual 2,3,7,8-substituted congeners, moisture content, organic carbon content (bed sediment only) and lipid content (fish tissue only). Data are available at http://oregon.usgs.gov/projs_dir/pn366/nawqa.html.

DIOXINS AND FURANS— Dioxin and furan analyses were performed by Quanterra Environmental Services (Sacramento, California) using isotope dilution gas chromatography/mass spectroscopy (EPA Method 8290, U. S. Environmental Protection Agency, 1990). For some sediment samples, the method was modified by increasing the sample mass to permit quantitation of low concentrations.

The author reviewed all ion chromatograms, associated calculations, and quality assurance data. Analytical results were within guidelines outlined in Method 8290. Some values, however, were reported by Quanterra as less than their minimum reporting level even though quantitation was allowable using Method 8290 detection criteria. Such values were recalculated by the author from the chromatographic data and are used in this analysis. They have somewhat greater uncertainty than larger values. The coefficient of variation generally was less than 25 percent for sediment samples and 30–40 percent for tissue samples.

MOISTURE, ORGANIC CARBON, AND LIPID CONTENT— Moisture and lipid content were determined by Quanterra Environmental Services as described in EPA Method 8290. Organic carbon content was determined by the USGS National Water Quality Laboratory (Arvada, Colorado) as the difference between total carbon and inorganic carbon (Methods O-5101-83 and O-5101-83, respectively [Wershaw and others, 1987]).

TABLE 4. Sampling summary.

[Dominant land use in basin or in immediate vicinity of site: I /U= industrial with urban, M=mixed use, A= agricultural, F= forested; tissue types: LSS=largescale sucker, CTT=cutthroat trout; * indicates triplicate samples; — indicates not sampled]

Map ID	Site Name	Land Use	Sampling Dates and Media	
			Bed Sediment	Tissue
1	Willamette River – RM 5	I/U	1992	—
2	Willamette River – RM 7	I/U	—	1992 – carp
3	Willamette River – RM 13	I/U	1992	—
4	Johnson Creek	M	1992	1992 – sculpin
5	Beaverton Creek	I/U	1992	—
6	Fanno Creek at Durham	I/U	1992	1992 – sculpin
7	Tualatin River at West Linn	M	1992	1992 – sculpin
8	Little Abiqua Creek	F	1993, 94*	—
9	Zollner Creek	A	1994	—
10	Pudding River at Aurora	A	1994*	—
11	Willamette River – RM 55	M	1992	1993 – LSS
12	Skookum Lake	A	1993	—
13	McKay Reservoir	A	1993	—
14	Yamhill River at Dayton	M	1992	—
15	Cedar Creek	F	1994	—
16	Middle Fourth Lake	I/U	1992	—
17	Willamette River – RM 137	A	1992, 95	1993, 95* – LSS
18	Mack Creek	F	1992	1992 – CTT
19	Amazon Creek	I/U	1992	1992 – bluegill
20	A-3 Channel	I/U	1992	—
21	Cottage Grove Lake	F	1993	—
22	Beaver Creek	M	1992, 94*	—
23	Fir Creek	F	1993	—

Overview of PCDD/F Concentrations

Bed sediment samples— Dioxins and furans were found in every bed sediment sample collected. Total PCDD/F concentrations varied widely across the basin, spanning nearly three orders of magnitude from 64 to 46,000 pg/g dry weight (fig. 3a). The highest concentrations were found at the most industrial sites, and the lowest concen-trations were found at forested sites. Total PCDD/F did not correlate well with organic carbon content, indicating that PCDD/F concentration is primarily determined by the strength and proximity of the sources.

The most toxic congener, 2,3,7,8-TCDD, was detected at only six sites (fig. 3b). Concentrations of 2,3,7,8-TCDD were usually less than 0.1 percent of the total PCDD/F. At A-3 Channel, the most contaminated site, the 2,3,7,8-TCDD concentration exceeded the low risk concentration limit for sensitive mammals. Detection of 2,3,7,8-TCDD did not appear to be related to total PCDD/F concentration or the type of site sampled. In samples that contained 2,3,7,8-TCDD, it accounted for 2–60 percent of the TEC.

Despite generally low 2,3,7,8-TCDD concentrations, TECs were high enough at some sites to be of concern. Eleven sites, including all of the industrial/urban sites, had TECs greater than the low risk concentration limit for sensitive mammals (2.5 pg/g; fig. 3c). Four of these sites, A-3 Channel, Middle Fourth Lake, Beaverton Creek, and Amazon Creek, had TECs that exceeded the low risk limit for sensitive birds (21 pg/g) and approached or exceeded the high risk criterion for sensitive mammals (25 pg/g). TEC in bed sediment at A-3 Channel exceeded the U.S. Centers for Disease Control criterion of 100 peq/g for human contact with soil, as well as the high risk criterion for fish.

Tissue samples— PCDD/Fs were found in all tissue samples. Total PCDD/F concentrations in fish tissue ranged from 3.2 to 50 pg/g wet weight (fig. 4a). The highest concentration in tissue occurred at a site with nearby upstream industrial inputs—Willamette River at RM 7; the lowest concentration in tissue occurred at a forested site— Mack Creek. Total PCDD/F concentration in tissue did not correlate well with lipid content. Total PCDD/F concentrations in fish tissue (expressed on a dry weight basis) were generally less than those in sediment obtained from the same site. PCDD/F concentrations in bed sediment and fish tissue were not well correlated, even after normalizing to organic carbon and lipid content, respectively. Some of the differences among tissue samples were likely due to differences among the species sampled and/or the ages of the individual fish, but it is unlikely that these factors alone could account for large differences between PCDD/F concentrations in fish and bed sediment.

Four of eight sites had detectable concentrations of 2,3,7,8-TCDD in tissue (fig 4b). At two sites, Willamette River at RM 7 and Johnson Creek, 2,3,7,8-TCDD concentrations in tissue exceeded the low risk concentration limit for sensitive mammals (0.7 pg/g). Two additional sites, Fanno Creek and Willamette River at RM 137, had TECs in tissue near the low risk limit (fig. 4c). No tissue samples had 2,3,7,8-TCDD concentrations or TECs that were likely to cause severe effects to aquatic life. No tissue samples had a TEC that exceeded human health criteria for fish consumption.

Comparisons with other studies— Results from this study are similar to those obtained by Curtis and others (1993), who measured 2,3,7,8-TCDD and 2,3,7,8-TCDF in bed sediment and tissue from six sites on the main stem Willamette River in 1990. They found the highest concentrations of these two congeners in both media at Portland Harbor (RM 6.8). They also found 2,3,7,8-TCDD concentrations in fish tissue at sites where it was not detected in bed sediment.

Fish tissue and/or bed sediment samples from four sites on the main stem Willamette River were also collected by the ODEQ for the National Bioaccumulation Study in 1987 (Eugene Foster, ODEQ, oral commun., 1998). They found higher concentrations of 2,3,7,8-TCDD in sediment from the Portland Harbor (about RM 7, 5.3 pg/g) than either this study (<0.8 pg/g) or the work by Curtis and others (1.6 pg/g). It is not known if the differences among these values reflect differences among precise sampling locations or if they are are an indication of declining concentrations. Neither of these other studies analyzed samples for non-2,3,7,8-substituted congener totals or for OCDD.

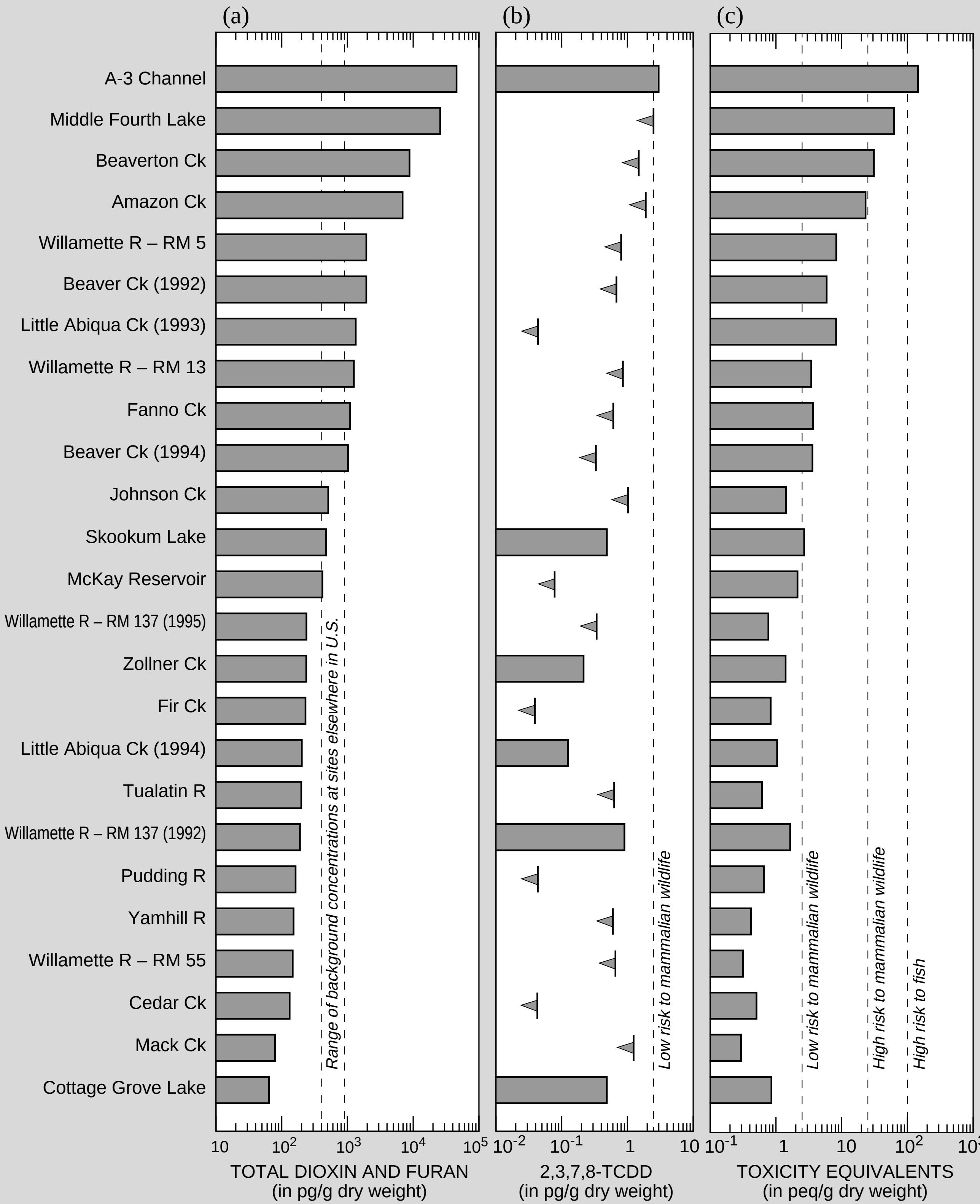

FIGURE 3. Concentrations of (a) total dioxins and furans, (b) 2,3,7,8-TCDD, and (c) toxicity equivalents in bed sediment. In (b), ◁ shows the detection limit when 2,3,7,8-TCDD was not detected. In (c), toxicity equivalents are calculated from dioxins and furans only. (See table 3 for definitions of risk criteria.)

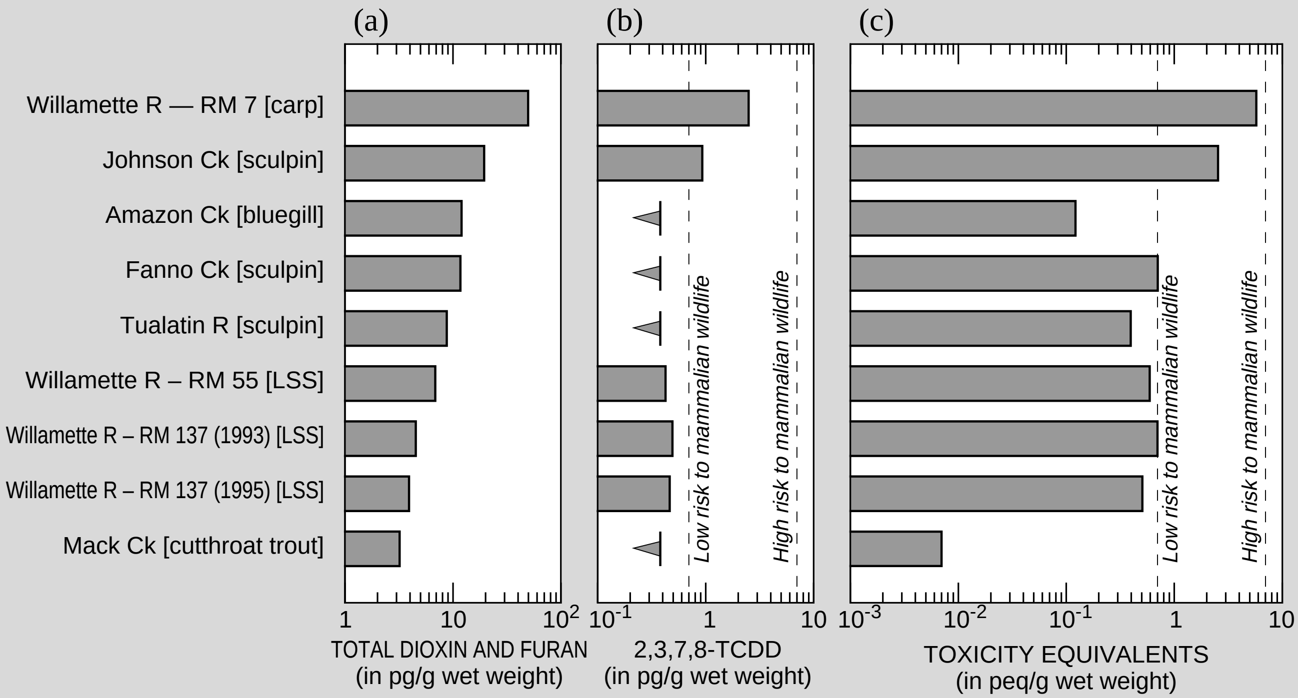

FIGURE 4. Concentrations of (a) total dioxins and furans, (b) 2,3,7,8-TCDD, and (c) toxicity equivalents in fish tissue. In (b), ◁ shows the detection limit when 2,3,7,8-TCDD was not detected. In (c), toxicity equivalents are calculated from dioxins and furans only. (See table 3 for definitions of risk criteria; LSS indicates largescale sucker.)

CONGENER PATTERNS

CHARACTERISTIC PATTERN IN BED SEDIMENT— Bed sediment samples throughout the basin had remarkably similar homolog compositions, regardless of their total PCDD/F concentrations (Bonn, 1998). Sediment PCDD/Fs were generally at least 80 percent dioxins. The dioxins were strongly dominated by the most highly chlorinated congeners. Typical dioxin composition was 77 percent OCDD, 19 percent HpCDD, 3 percent HxCDD, and about 0.3 percent each PeCDD and TCDD. The furan pattern was similar to, but not as strong as the dioxin pattern.

Because the congeners that account for most of the PCDD/F in sediment (OCDD, HpCDD, OCDF, and HpCDF) are also the least toxic, the TECs are substantially less than the total PCDD/F concentrations (fig. 3a and c). The congener concentration profiles are similar enough among Willamette Basin bed sediment samples that the TEC can be estimated from total PCDD/F using:

$TEC = (0.003) \times total\ PCDD/F + 0.3$ (r^2=0.96, p=0.0001).

PATTERN COMPARISONS BETWEEN BED SEDIMENT AND TISSUE—

Congener patterns in tissue and sediment were not generally similar. Figure 5 shows congener concentration patterns in bed sediment and tissue from Johnson Creek; other sites have similar patterns. Total PCDD/F concentrations in tissue were lower than those in bed sediment from the same site. However, concentrations of the most toxic compounds— congeners with four or five chlorine substitutions and 2,3,7,8-substituted congeners were generally higher in tissue than in sediment from the same site. Tissue samples from three sites had detectable 2,3,7,8-TCDD even though it was not detected in their associated sediment samples. The different congener pattern in tissue resulted in tissue TECs exceeding sediment TECs at more than half of the sites where both media were analyzed.

The reasons for the different congener patterns in fish tissue and sediment are unknown. Simple partitioning into organic carbon and lipid does not account for the difference. Fish tissue may preferentially accumulate specific congeners, such as 2,3,7,8-congeners; alternatively, fish may metabolize or excrete highly chlorinated congeners, such as OCDD. Changes in congener patterns within the food chain, could also result in the accumulation of specific congeners.

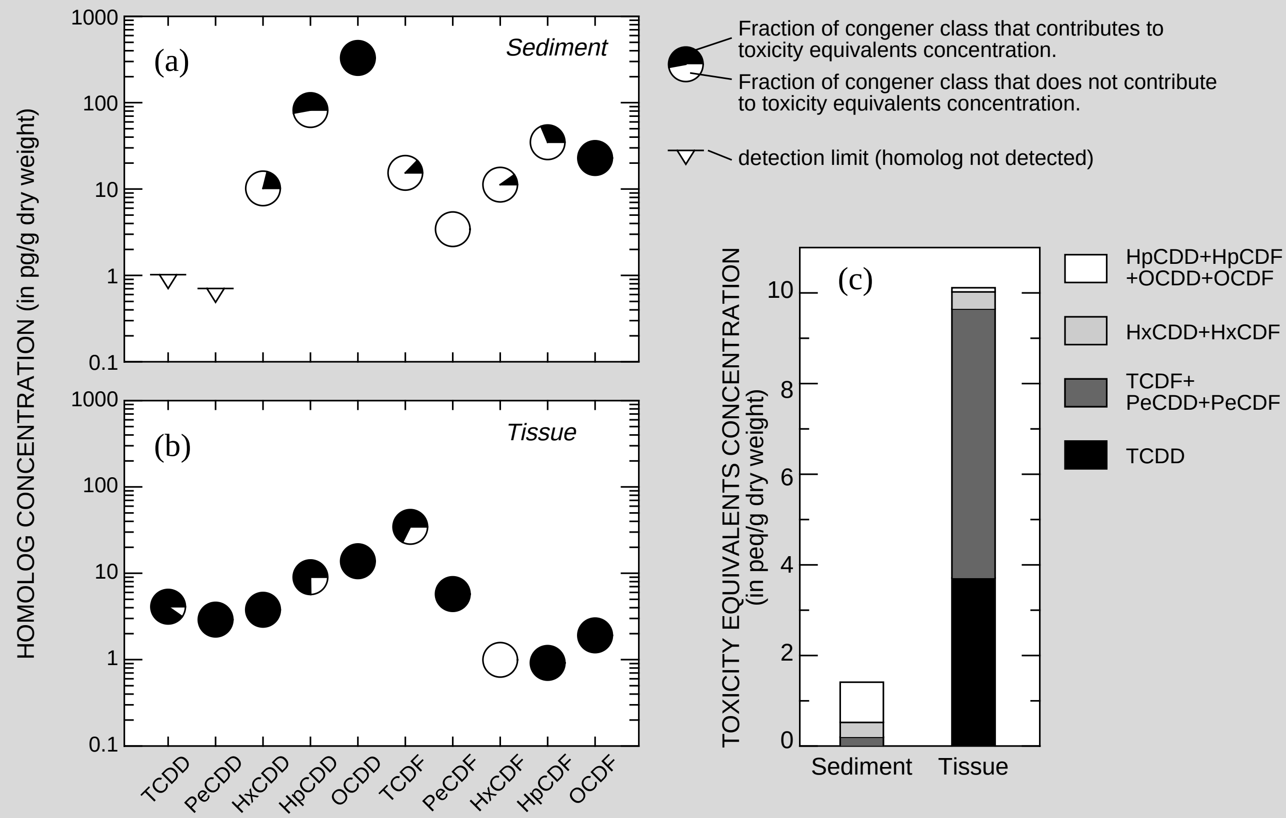

FIGURE 5. Congener concentration patterns in (a) bed sediment and (b) fish tissue (sculpin) at the Johnson Creek site. The associated toxicity equivalents concentrations are compared in (c). Compound groupings in (c) are based on similarity of chlorine substitutions and toxicity equivalence factors (see table 2). Note that concentrations in tissue are expressed on a dry weight basis rather than wet weight as in figure 4.

RELATING CONGENER PATTERNS TO SOURCES— Several papers have described the use of PCDD/F congener patterns as “fingerprints” to identify specific sources (Eitzer, 1993; Fattore and others, 1997; Fiedler and others, 1996; Horstmann and McLachlan, 1995; Rose and others, 1994). This approach has had mixed success. Because of the similarity among the congener patterns in the Willamette Basin, congener “fingerprints” are, at best, of limited use in local source identification. Some potential associations were found, however.

Dioxin congener patterns and the total PCDD/F concentrations suggest that atmospheric deposition is the predominant source of PCDD/Fs at agricultural and forested sites (fig. 6a, b). The dioxin congener patterns at all agricultural and forested sites were essentially the same and were similar to dioxin congener patterns found at reference sites throughout the world (Hites, 1990; Rose and others, 1994). Total PCDD/F concentrations at agricultural and forested sites were not statistically different from one another (α=0.1) and were less than or similar to background concentrations at reference sites elsewhere (400 – 900 pg/g) where atmospheric deposition has been the presumed source. Two sites were located in protected watersheds (Fir Creek, site 23, is in the Bull Run watershed and Mack Creek, site 18, is in the H.J. Andrews Experimental Forest) where there have been no known sources other than atmospheric deposition (Doug Bloem, Portland Water Bureau, oral commun., 1998; Art McKee, U.S. Forest Service, oral commun., 1998).

Industrial/urban sites were distinguished from agricultural and forested sites by higher total PCDD/F concentrations and a slightly different dioxin congener pattern (fig. 6c). Congener patterns at industrial/urban sites were characterized by relatively higher concentrations of hepta- and octa-congeners. For example in figure 6, the TCDD concentration was about 10 times higher at the industrial/

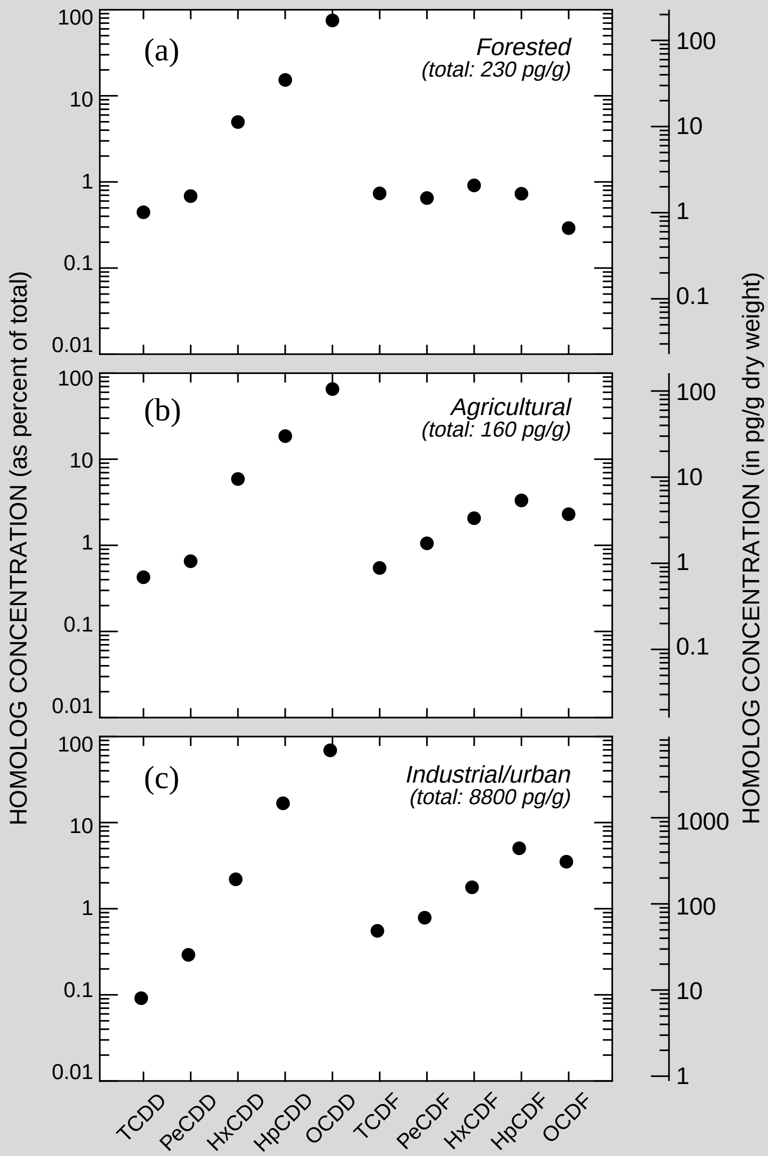

FIGURE 6. Congener concentration patterns in bed sediment at representative sites: (a) forested (Fir Creek), (b) agricultural (Pudding River), and (c) industrial/urban (Beaverton Creek). Absolute concentrations are shown on the far right scales.

urban site than at the forested or agricultural sites; in contrast the OCDD concentration was 50 times higher. In general, at industrial/urban sites, OCDD concentrations were about three orders of magnitude higher than the TCDD concentrations, whereas at forested and agricultural sites, OCDD concentrations were only about two orders of magnitude higher than TCDD concentrations. An association between highly chlorinated congeners (especially OCDD) and pentachlorophenol has been reported in the literature, suggesting that pentachlorophenol-related inputs may be an important source of PCDD/F at industrial sites (Hagenmaier and Brunner, 1987). Samples from this study were not analyzed for pentachlorophenol, however, so such an association is speculative at this time.

Two sites, Little Abiqua Creek (site 8, a forested site) and Middle Fourth Lake (site 16, an industrial/urban site), had unusual furan patterns that may indicate distinct sources. When Little Abiqua Creek was sampled in 1993, the sample included bed sediment taken from under a wooden bridge. This sample had unusually high levels of furans—especially TCDF, PeCDF and HxCDF. Little Abiqua Creek was resampled (in triplicate) in 1994, but in contrast to the 1993 sample, the 1994 sample was obtained upstream from the bridge. The high furan concentrations were absent in the 1994 samples (fig 7). The furans in the 1993 sample may have been associated with preservatives used to treat the bridge.

Middle Fourth Lake bed sediment had unusually high concentrations of OCDF. Reports of OCDF-dominated PCDD/F concentration patterns are somewhat unusual in the literature. The source of the OCDF at Middle Fourth Lake is not known. This sample did contain a variety of other contaminants including polyaromatic hydrocarbons (total PAH > 1 µg/g), polychlorinated biphenyls (total PCB = 1.7 µg/g), and hexachlorobenzene (0.13 µg/g) (Harrison and others, 1995).

The Willamette River site at RM 137 is about 10 miles downstream from a pulp and paper mill that used elemental chlorine to bleach wood pulp, a process that is associated with 2,3,7,8-TCDD production. In 1993, the paper mill reduced its use of elemental chlorine by 40 percent and implemented other changes that resulted in the elimination of elemental chlorine bleaching in 1996 (Art Vosburg, Pope and Talbot, Inc., written commun., 1998). The 1992 bed sediment sample from this site had the second highest 2,3,7,8-TCDD concentration among all sites (0.9 pg/g); total PCDD/F, however, ranked 19th. In contrast, 2,3,7,8-TCDD was not detected (<0.3 pg/g) in the 1995 bed sediment sample. Although bed sediment data suggest a decline in 2,3,7,8-TCDD between 1992 and 1995, concentrations in fish tissue from 1993 and 1995 were not different within analytical variability.

Implications for Monitoring and Management

Dioxins and furans were ubiquitous in bed sediment sampled throughout the Willamette Basin during this study; monitoring studies will probably find these compounds in all bed sediment samples. In addition, because congener patterns were similar among sites, it is reasonable to assume that all congeners, including 2,3,7,8-TCDD, are present in sediment throughout the basin and will be detected if detection limits are low enough. This low-level, background PCDD/F is an important factor to consider when designing strategies to evaluate and manage PCDD/F contamination.

Background concentrations of total PCDD/Fs in Willamette Basin bed sediment sampled during this study were on the order of 200 pg/g dry weight. Most of this was probably due to atmospheric deposition. Because these compounds are long lived in sediment, it is unlikely that substantial decreases in bed sediment concentrations will be seen in the near future. Background TECs in bed sediment were less than 1 peq/g dry weight.

When possible, sediment monitoring strategies should include the full suite of tetra- through octa-congeners rather than being limited to 2,3,7,8-TCDD alone. Because the hepta- and octa- congeners generally account for 30-60 percent of the TEC in bed sediment, using 2,3,7,8-TCDD concentration alone substantially underestimates the TEC in most bed sediment samples. In addition, examination of the congener pattern may help identify sources in some cases.

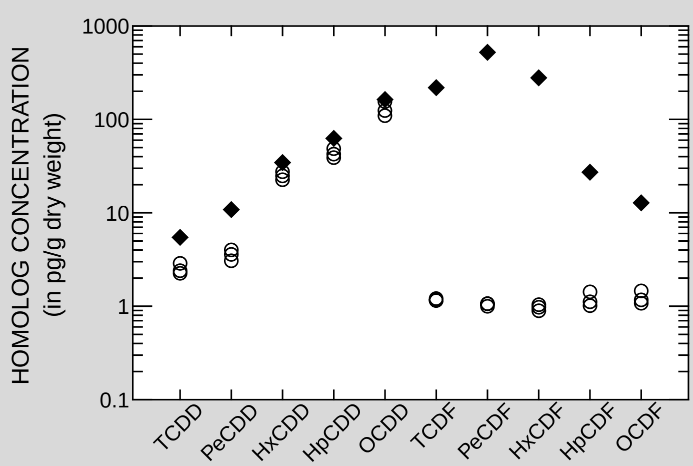

FIGURE 7. Congener class concentrations in bed sediment at Little Abiqua Creek in 1993 (◆) and 1994 (○).

Because congener patterns differ between bed sediment and fish tissue, neither medium is an adequate substitute for the other. In particular, TECs in fish tissue may be higher than TECs in sediment from the same site. Monitoring PCDD/F concentrations in the water column, in suspended sediment, and in wet and dry atmospheric deposition should also be considered in order to better assess the transport or bioavailability of these compounds. Food chain studies could also be considered to help determine pathways for the accumulation of PCDD/Fs in fish and other organisms.

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